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Degradation of root exudates in closed hydroponic systems using UV/H_2O_2: Kinetic investigation, reaction pathways and cost analysis

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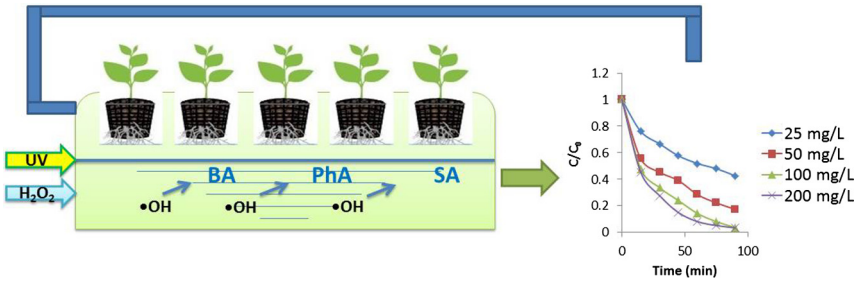
HIGHLIGHTS

- The degradation rate of BA was faster than that of PhA and SA
- The majority of organic acids transformed into byproducts rather than complete mineralization
- Degradation of organic acids was significantly hindered in presence of inorganic ions
- The oxidant (H_2O_2) concentration plays the most significant role in total cost during the oxidation process

GRAPHICAL ABSTRACT



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ABSTRACT

Qualitative screening of reused nutrient solution (RNS) displays the presence of several organic acids. In this study, the degradation by UV/H_2O_2 of three of those organic acids (benzoic (BA), phthalic acid (PhA) and succinic acid (SA)) present in RNS was investigated. The results indicated that (i) the degradation rate of BA was faster than that of PhA and SA and (ii) by increasing the contact time the degradation of all acids was improved. For example, the removal of BA increased from 83% and 91% when increasing the contact time from 90 min to 270 min in the presence of 50 mg L^{-1} and UV. A maximum COD (30%) and UV_{254} (68%) removal were obtained when 200 mg L^{-1} H_2O_2 was applied for 90 min. No significant change was observed in terms of parameters such as PO_4^{3-} and NO_3^- while electrical conductivity (EC) and pH were slightly changed during the oxidation process. Pseudo- first -order represented well the experimental data for the degradation of the selected organic acids in RNS (particularly for BA and PhA), exhibiting high linear correlation coefficients ($R^2 \geq 0.96$). Moreover, the results showed that the decomposition of organic acids was significantly influenced in the presence of inorganic ions in RNS. GC–MS analysis revealed the presence of several intermediate products during the oxidation process and the primary reaction pathway of benzoic acid was accordingly proposed. Finally, a bench scale cost investigation showed that low concentration H_2O_2 (50 mg L^{-1}) in longer time (270 min) is more cost effective than high concentration H_2O_2 (200 mg L^{-1}) in a shorter time (90 min).

1. Introduction

Increasing demand for fresh water from population growth, drought and climate change is the common issue in the most parts of the world

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(Bates et al., 2008) and has necessitated greater attention to the conception of water reuse. Agriculture is believed to be a prime freshwater consumer representing approximately 70% of the water demand (WWAP, 2012). Recently, increasing water demand for different purposes in domestic, industrial, environmental, and recreational sectors has forced farmers to manage irrigation water carefully, contributing to environmental preservation. This demand has resulted in the shift from conventional soil-bound and open hydroponic to closed hydroponic systems (Lee et al., 2017; Trejo-Téllez and Gómez-Merino, 2012). Today, hydroponic as a type of controlled environment agriculture is being extensively used in commercial greenhouse vegetable production worldwide. This type of farming is advantageous with respect to efficient use of water, land and energy, resulting in a cost-effective and environmentally-friendly system (Trejo-Téllez and GómezMerino, 2012). Furthermore, this system provides better control of climate and diseases surrounding the roots. Despite the growing interest in hydroponic cropping systems, some vital factors such as plant diseases, root exudates occurrence and changes in nutrient solution composition have to be taken into account (Hosseinzadeh et al., 2017).

One of the greatest concerns regarding closed hydroponic systems is the potential spread of root infectious diseases where the presence of even one infected plant will jeopardize the entire crop health (Postma et al., 2008). To minimize the risk of root pathogen dispersal in closed loop systems, the nutrient solution has to be disinfected prior to reuse. In this respect, various techniques such as heat treatment, ozonation, hydrogen peroxide, chlorine, UV radiation, membrane filtration and slow sand filtration have already been investigated (Runia, 1993). All the advantages and disadvantages of these techniques have been extensively reviewed by Ehret et al. (2001).

In a few studies, however, the efficacy of hydrogen peroxide for control of waterborne plant pathogens in closed cropping systems has been examined (Table 1). Recent studies on this topic have shown that low concentrations of H_2O_2 are not able to remove all pathogens effectively. On the other hand, higher doses of H_2O_2 might result in phytotoxicity. According to the literature, phytotoxicity thresholds for hydrogen peroxide in the nutrient solution have been determined in the range of 8 mg L^{-1} for lettuce to 125 mg L^{-1} for cucumber. This indicates that phytotoxicity threshold may vary for different crops. To overcome this issue, it is highly recommended to apply the oxidizing agents (i.e. H_2O_2) into the source water supply (not directly to the nutrient solution in the system). Furthermore, it should be noted that the optimum concentration of H_2O_2 should be applied to ensure that is fully consumed during the oxidation process and no residual H_2O_2 remains in RNS.

Autotoxicity is another important factor which usually occurs once a plant emits several toxic chemical compounds (i.e. organic acids) into the aqueous solution, resulting in a delayed germination and growth inhibition of the same plant species (Miller, 1996). Several experimental studies have been reported about the adverse effect of root exudates and autotoxicity on the plant performance during the cultivation in closed hydroponic systems (Hosseinzadeh et al., 2017a). In this regard, several techniques such as ozonation, activated carbon adsorption, TiO_2 photocatalysis, electrodegradation and membrane filtration have been developed to mitigate the autotoxicity revealed in closed hydroponic systems (Hosseinzadeh et al., 2017a).

Nowadays, Advanced Oxidation Processes (AOPs) have gained considerable attention due to effective organic decomposition from wastewater (Liu et al., 2018; Oloibiri et al., 2015). AOPs generate highly reactive oxidizing free radicals, (especially ·OH) which attack the recalcitrant organic chemical compounds, often completely mineralizing them into CO_2 and H_2O or converting them into less harmful or lower chain compounds (Chys et al., 2015). According to the literature, several carboxylic acids such as benzoic and phthalic acids were detected in RNS which hindered the germination and plant growth (Hosseinzadeh et al., 2017a). Recently, a limited number of studies on the photocatalytic treatment of RNS using TiO_2 (Miyama et al., 2013; Qiu et al., 2013) and ozonation (Hosseinzadeh et al., 2017b) have been reported. Although some researches have been devoted to investigating the performance of H_2O_2 on pathogens control, no attempt has been made yet to examine the effect of H_2O_2 on decomposition and removal of organic acids in RNS, to the best of our knowledge. Therefore, this work aims to investigate the transformation of those harmful compounds to some intermediates which may have less or no adverse impact on growth and yield by means of ·OH produced by UV/H_2O_2. In this approach, the degradation pathway of the benzoic acid as an indicator is proposed and degradation of the main intermediate is subsequently investigated to figure out whether the formed intermediate is completely or partially removed during the oxidation process.

Indeed, in order to extend the lifespan of recirculating nutrient solution in the closed hydroponic systems, it is important to identify and control the fate of those compounds present in RNS, leading to promote the sustainability in modern agricultural systems.

As such, the aims of this study are to (1) investigate the potential effect of UV/H_2O_2 on degradation or removal of root exudates (in particular BA, PhA and SA), (2) evaluate the effect of inorganic ions on degradation rates by performing experiments in DI water, (3) enhance the efficiency of UV/H_2O_2 process through applying the optimum H_2O_2 dose and reaction time in order to reduce the energy cost for the removal of root exudates from RNS in bench scale, and (4) identify the byproducts formed during the oxidation process and propose the hypothetical degradation pathway.

2. Material and methods

2.1. Chemicals

BA, PhA and SA, acetonitrile (ACN), methanol and water (HPLC grade) were supplied by Sigma-Aldrich (Belgium). Catalase from bovine liver (lyophilized powder, 2000–5000 units/mg protein) and hydrogen peroxide (H_2O_2, 30 wt%) were purchased from Sigma-Aldrich (Belgium). All the above chemicals were of analytical grade (purity of 98% or above) and used without further purification.

2.2. RNS sampling

Experiments were conducted using RNS samples from a lettuce greenhouse (hydroponic) company, as described elsewhere (Hosseinzadeh et al., 2017b). In order to minimize chemical and biological changes, the sample (100*L*) was kept at the temperature of 4 °C and

Table 1
Performance of hydrogen peroxide for inactivation of plant pathogens in closed hydroponic systems.

Type of organism	H_2O_2 dosage (mg L^{-1})	Time (min)	Efficiency (%)	Ref
Phytophthora	185	1	100%	Steddom and Pruett (2012)
Bacillus subtilis	N/A	360	100%	Van Wyk et al. (2012)
Pythium spp.	12.3	N/A	100%	Choppakatla (2009)
Fusarium foetens	135	15	100%	Elmer (2008)
Fusarium	34	N/A	100%	Abdou and Galal (1997)
Tomato mosaic virus	400	N/A	99.97%	Runia (1993)
Fusarium oxysporum f.	100	5	100%	Runia (1993)

Table 2
Characteristics of the water sample (RNS).

Parameter	Range
pH	5.7–5.9
Conductivity (μS cm^{-1})	2120–2230
NO_3^--N (mg L^{-1})	21–23
PO_4^{3-}-P (mg L^{-1})	10–11
COD (mg L^{-1})	80–103

filtered using cotton wool to separate out any solid particles prior to use for the experiments. The characterization of RNS is summarized in Table 2.

2.3. Treating RNS samples and experimental design (UV/H_2O_2)

Initially, a screening of organic acids in RNS by GC–MS was performed and several compounds were identified (Hosseinzadeh et al., 2019). In order to evaluate the performance of UV/H_2O_2, three components (BA, PhA and SA) were chosen as target compounds (Table 3). According to literature, these acids have shown a potent inhibitory effect on germination and plant growth (Hosseinzadeh et al., 2017a). In this study, the initial concentration of these acids was almost 1.6 mg L^{-1}, 4.9 mg L^{-1} and 0.7 mg L^{-1} for BA, PhA and SA respectively. Additionally, to make a uniform RNS, the initial concentration of these acids was adjusted to 25 mg L^{-1} by spiking these acids into the sample. It should be noted that each acid was spiked into the sample separately (25 mg L^{-1} BA, PhA or SA). Within the oxidation experiments, different H_2O_2 doses (25, 50, 100, 200 and 400 mg L^{-1}) were applied to assess the degradation efficiency of target acids. Analytic samples (2 mL) were withdrawn at known intervals (15 min) and immediately analyzed using HPLC. Further analyses (i.e. EC, pH, UV_{254} and COD) were carried out in order to obtain a deeper understanding of UV/H_2O_2 effect on the mineralization, pH changes and root exudates (in particular carbon-based compounds) removal during the oxidation process.

The removal efficiency of organic acids (E) through the UV/H_2O_2 process is defined as

$$E(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of organic acid in the solution (mg L^{-1}), C_t is the concentration of organic acid in the solution at time t.

The presence of H_2O_2 interferes with COD analysis since it is able to consume the oxidation agents (i.e. $K_2Cr_2O_7$) (Talinli and Anderson, 1992) resulting in an overestimation of the COD measurements. Therefore, in this study, catalase was used to eliminate the residual H_2O_2 present in the sample. In this approach, the catalase stock solution was prepared and renewed every day to ensure its activity and high efficiency for quenching residual hydrogen peroxide. 0.2 mg L^{-1} catalase was introduced into each sample based on the findings reported by Liu et al. (2003) indicating a rapid decay of H_2O_2 (142 mg L^{-1}) occurs in <10 min with no impact on byproducts (DBP) formation. All quench tests were performed at ambient temperature. After the scavenging process for all the samples, COD and UV–Vis analyses were subsequently carried out as described below.

Table 3
Physico-chemical characteristics of the target root exudates.

Name	Molecular weight (g/mol)	Molecular Structure	Solubility in water at 25 °C
Benzoic acid	122,12		3400 mg L^{-1} [a]
Phthalic acid	166,13		7010 mg L^{-1} [a]
Succinic acid	118,09		83,200 mg L^{-1} [b]

[a] Yalkowsky and Dannenfelser (1992).
[b] Yalkowsky and He (2003).

2.4. Experimental setup

Photodegradation experiments were conducted using a batch cylindrical photoreactor filled with 750 mL of RNS sample at room temperature. The reactor was equipped with a low-pressure mercury vapor lamp (18 W, UV-C manufactured by Oase, Germany) (Chys et al., 2015) located in the center of the reactor and emitting at 254 nm (Fig. 1). The UV lamp (UV intensity of 1150 μW·cm^{-2}) was switched on to initialize the photocatalytic process for 15 min. RNS and DI water containing 25 mg L^{-1} of benzoic, phthalic or succinic acids were used in this study. During the initialization, a desired amount of H_2O_2 was introduced into the feed tank containing 1 L of the sample. Thereafter, the RNS sample and DI water were pumped with a peristaltic pump (DULCO®flex DF4a – ProMinent) through the photoreactor at a flow rate of 3 L h^{-1}. The overall experiment lasted for 90 min (unless otherwise stated) and during the experiment, the sample was agitated by a magnetic stirrer to maintain the homogeneity. All experiments were performed in triplicate and the mean values were used for the data analysis.

2.5. Instruments and analytical determinations

Water sample preparations (extraction and derivatization) were carried out according to our previous research (Hosseinzadeh et al., 2017b) prior to GC–MS analysis. For qualitative screening, GC–MS analysis was subsequently performed using an Agilent 6890 GC Series (Agilent Technologies, Palo Alto, CA, USA) gas chromatograph coupled with a Hewlett Packard 5973 mass selective detector. The GC was equipped with an HP5 capillary column (30 mm length, 0.25 mm inner diameter, 25 μm film) with He as the carrier gas (1 mL min^{-1}). The analytical procedure was carried out based on the chromatographic conditions previously described elsewhere (Hosseinzadeh et al., 2017b; Lee et al., 2006).

For quantitative measurement, organic acids were analyzed using an Agilent HPLC system, model 1100 equipped with a quaternary solvent pump, thermostatted column compartment, degasser, autosampler, a 200 μL injection loop, a UV-detector. Alltima C18, 5 μm analytical column (250 mm × 4.6 mm i.d.) (Alltech) was used as a stationary phase. Agilent ChemStation software (Hosseinzadeh et al., 2017b) was employed to process the data. HPLC analysis was carried out to determine the concentration of the selected organic acids (BA, PhA and SA). In this regard, two different methods were employed as follows:

For BA and PhA analysis: a mobile phase including an isocratic elution of acetonitrile and water (40:60; *v*/v, pH adjusted to 2 with phosphoric acid) was delivered at a flow rate of 1.0 mL min^{-1} at room temperature. For SA analysis: an isocratic elution of acetonitrile and water (5:95; v/v, pH adjusted to 2.5 with phosphoric acid) was delivered at a flow rate of 1.0 mL min^{-1} at room temperature.

All samples were filtered through a 0.45 μm membrane filter prior to HPLC analysis. Standard solutions were injected to obtain the retention time for each compound. The concentration of the different compounds was calculated based on the external standard method.

The pH and electrical conductivity (EC) of the raw and treated RNS were measured using a Hach HQ 40d multimeter at 25 °C. Analysis of chemical oxygen demand (COD) (Clesceri et al., 1999), nitrate (NO_3^--N) and phosphate (PO_4^{3-}-P) concentrations were conducted with Hach (Hach, Belgium) cuvettes and DR2800 spectrophotometer based on the standard methods (Hach, 2002). The absorbance at 254 nm was recorded on a Shimadzu 1600 spectrophotometer equipped with quartz cuvettes (1 cm × 1 cm cross-section).

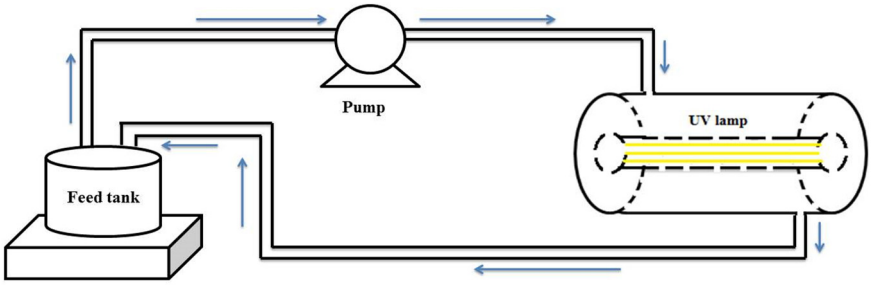

Fig. 1. Schematic diagram of UV-C photoreactor.

3. Results and discussion

3.1. Root exudates (organic acids) detected in the RNS

Qualitative analysis (GC–MS) revealed the presence of 14 organic acids in the RNS before treatment. Benzoic, succinic, glutaric, adipic, lauric, azelaic, myristic, myristoleic, palmitic, phthalic, palmitoleic, stearic, margaric and oleic acids were identified. In order to investigate the performance of UV/H_2O_2, BA, PhA and SA were chosen (as example components) for further analyses (i.e. HPLC, COD, EC, pH, nitrate and phosphate). It is noteworthy that, the potent inhibitory effect of these organic acids (particularly BA) on growth and yield of different crops has been reviewed previously (Hosseinzadeh et al., 2017a).

3.2. The variation in common parameters

In order to meet the optimum uptake rate of essential elements by the root of plants in the RNS, the pH value must fall in the appropriate range. According to literature, the optimum pH for growing crops such as lettuce in hydroponic systems ranges between 6 and 6.5 (Morgan, 1998). If the pH value deviates from this range, it has to be adjusted by adding a strong acid or base to maintain the pH level within the desired range. In this study, the pH values of spiked RNS before any treatment were 5.94 (25 mg L^{-1} BA), 5.8 (25 mg L^{-1} PhA) and 5.84 (25 mg L^{-1} SA) indicating that the pH is a little out of the desired range however this might be compensated by a strong base. The pH values were slightly decreased in the exposure of UV/H_2O_2 for all experiments whereas the pH value reached 5.72, 5.62 and 5.65 for BA, PhA and SA respectively in presence of 200 mg L^{-1} H_2O_2. This finding can be attributed to the assumption that more carboxylic acids are formed during the oxidation process as also evidenced by Hosseinzadeh et al. (2017b).

Electrical conductivity (EC) is known to be one of the most important parameters for successful hydroponic production as it indicates the total nutrient concentration in nutrient solution indirectly. The optimum level of EC for successive hydroponics was estimated to be in the range of 1.5–2.5 dS m^{-1}. Since inappropriate EC level may enhance the risk of toxicity in RNS, hence it is recommended to monitor the concentration of inorganic ions regularly and maintain the EC value in the desirable range. In this study, a slight variation in EC values was observed by applying different concentration of H_2O_2 after 90 min. The initial EC value was ranged between 2120 and 2230 μS cm^{-1} while this value was decreased to 2048 μS cm^{-1}after 90 min irradiation in the exposure of 200 mg L^{-1} H_2O_2. This fact might be attributed to the poor mineralization yielded during the oxidation process. In fact, the contribution of diverse inorganic ions in scavenging of ·OH radicals do not allow the several intermediates to transform into CO_2 and H_2O efficiently resulting in small mineralization. The values of PO_4^{3-} and NO_3^- remained almost unchanged during the 90 min oxidation process.

3.3. COD and UV–vis analyses

As shown in Fig. 2, with increasing the H_2O_2 concentration from 25 to 200 mg L^{-1}, the COD removal efficiency was improved whereas this value increased from 11.6% to 30.1% (RNS, 25 mg L^{-1} BA), 7.5% to 23.6% (RNS, 25 mg L^{-1} PhA) and 7.3% to 20.7% (RNS, 25 mg L^{-1} SA). As a result, this value was found to be relatively low (<30%) for all the experiments within 90 min irradiation which is presumably connected with the presence of inorganic ions in the RNS which are able to react with hydroxyl radicals formed during the oxidation process, leading to incomplete mineralization. Moreover, it is worth noting that, COD removal efficiency for BA spiked sample was obtained to be higher than others. This finding can be attributed to the higher decomposition rate of BA in comparison with PhA and SA.

UV–vis analysis was performed to enable an improved understanding of the effect of UV/H_2O_2 on the absorbance removal particularly in the range of 250 to 300 nm. Generally, RNS consists of a mixture of inorganic ions and organic compounds released from the root of the plants (Hosseinzadeh et al., 2017a). Some inorganic anions are able to absorb peaks in the UV wavelength range. For example nitrogen species such as nitrate are known to absorb UV below 250 nm (Armstrong, 1963).

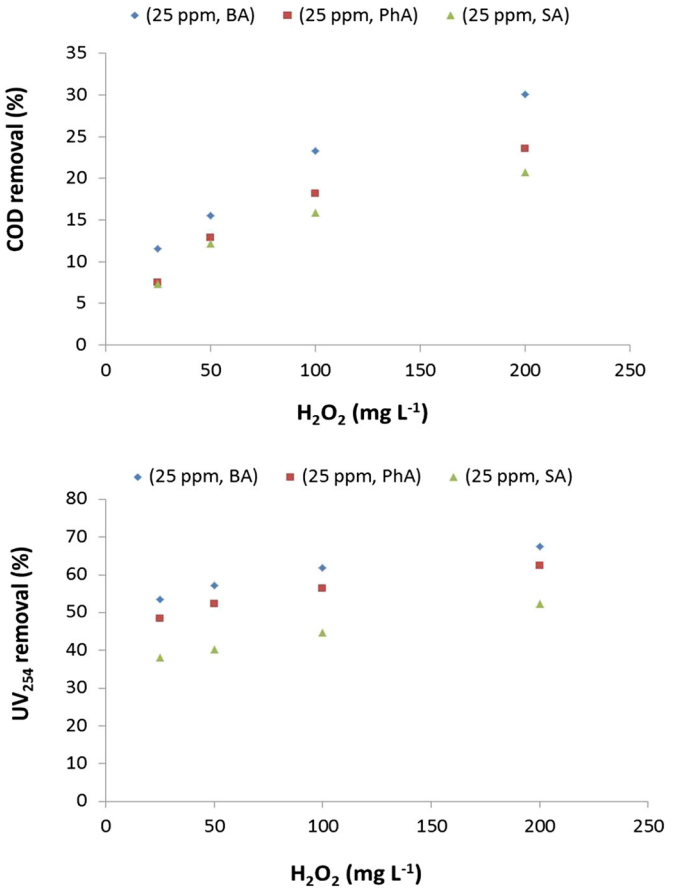

Fig. 2. Effect of H_2O_2 concentration on COD and UV_{254} removal during UV/H_2O_2 treatment of RNS after 90 min.

Therefore the absorbance value of organic compounds at shorter wavelengths (<250 nm) is therefore likely to suffer from interferences. The maximum absorbance removal was observed from 250 to 300 nm. The UV absorption at 254 nm was specifically measured (for raw and treated RNS) as it is known to represent aromatic and double-bond compounds (Dickenson et al., 2009). The results showed that the UV_{254} decreased from 1.052 $cm^{-1}$for raw RNS to 0.341 cm^{-1} in the presence of UV and 200 mg L^{-1} H_2O_2 (Fig. 2). It is necessary to highlight the fact that the difference between COD (30.1%) and UV_{254} (67.6%) removal after 200 mg L^{-1} UV treatment might prove the incomplete mineralization after 90 min. It is assumed that during the oxidation process large compounds (i.e. aromatics) were broken down into smaller carbon-based molecules which are not able to absorb UV_{254}, therefore, less COD removal was expected.

3.4. Degradation of benzoic, phthalic and succinic acids

3.4.1. Effect of H_2O_2 dose

Fig. 3 reveals the effect of different H_2O_2 dosages on the decomposition of BA, PhA and SA (in DI water and RNS) respectively within the irradiation time of 90 min. As shown in Fig. 3, within 90 min, all acids at different concentrations of H_2O_2 could be effectively degraded indicating the presence of hydroxyl radicals during the reaction. The rate of acids decomposition is faster in the early stage of the reaction than in the later stage (particularly in DI-water). It was also found that the removal efficiency of BA is quite higher than PhA and SA. The results also showed that, with the increasing of H_2O_2 dosage from 25 to 200 mg L^{-1}, the removal efficiency was increased from 58% to 97% for BA, 23% to 71% for PhA, 30% to 56% for SA. The increased acids removal is attributed to an increase in the hydroxyl radical concentration generated during UV/H_2O_2 system (reaction (2)). However, a further increase of H_2O_2 concentration (800 mg L^{-1}) showed an adverse effect on the removal efficiency of the acids (data not shown). For example, the removal efficiency of benzoic acid was reduced from 97% in the presence of 200 mg L^{-1} H_2O_2 to 78% after applying 800 mg L^{-1} H_2O_2 in 90 min. This occurrence can be explained by the fact that once H_2O_2 is applied in excess, hydroxyl radical efficiently reacts with H_2O_2 and produces HO_2 radical ($k = 2.7 \times 10^7$ M^{-1} s^{-1}) (reaction (3)). On the other hand, excessive ·OH radicals might dimerize to H_2O_2 ($k = 5.5 \times 10^9$ M^{-1} s^{-1}) (reaction (5)). This undesirable reaction might compete with the degradation of the target compounds, therefore, it is crucial to optimize the operating conditions (particularly H_2O_2 concentration) for

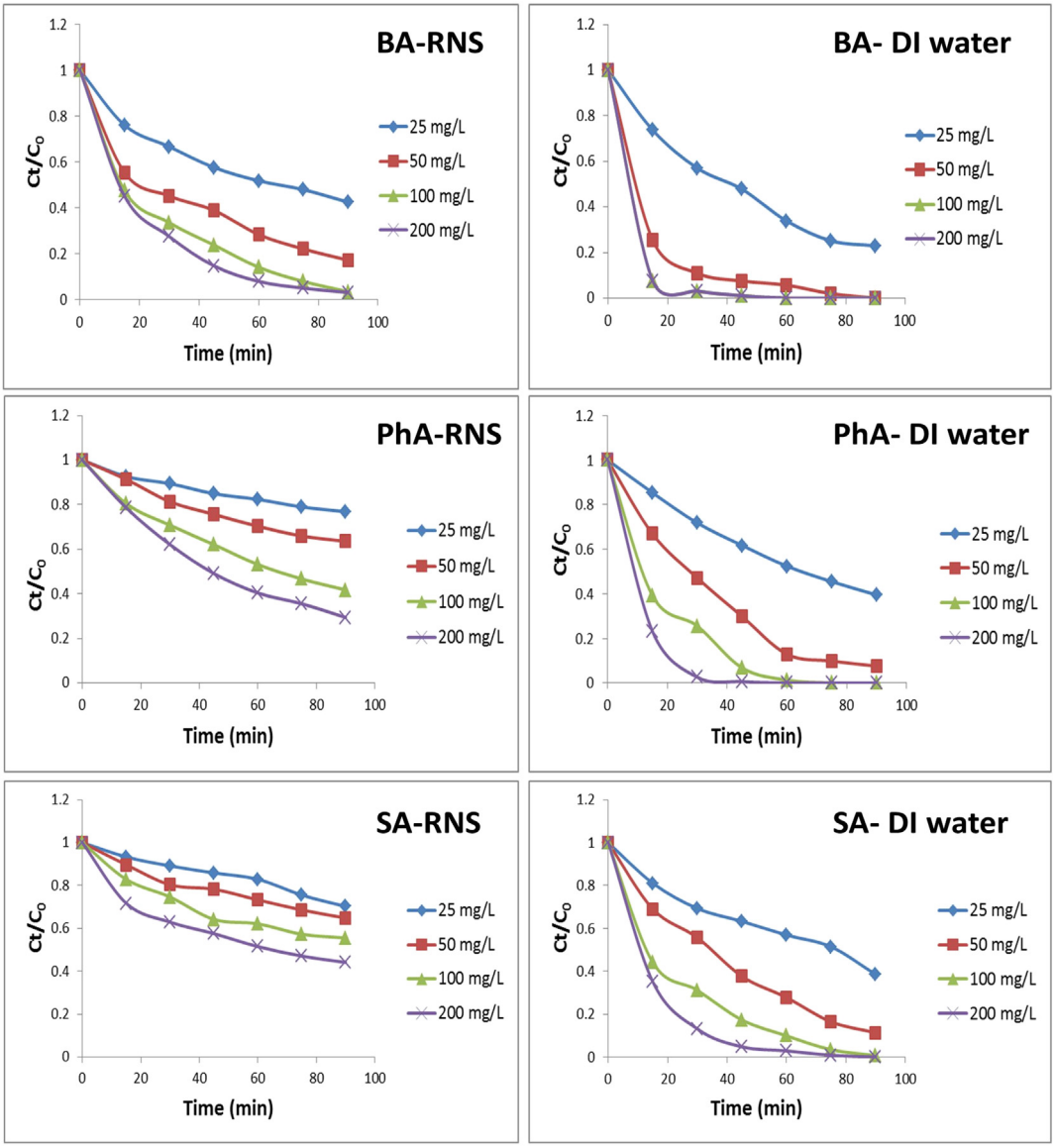

Fig. 3. Effect of H_2O_2-UV treatment at different H_2O_2 doses on BA, PhA and SA degradation in RNS and DI-water.

an efficient photo-decomposition of UV/H_2O_2 and avoid an excess of reagent that might delay the degradation process (Liu et al., 2018).

$$H_2O_2 + hv \rightarrow 2 \cdot OH2003 \quad (2)$$

$$HO_2 \cdot + \cdot OH \rightarrow O_2 + H_2O \text{ (Buxton et al., 1988)} \quad (3)$$

$$HO_2 \cdot + \cdot OH \rightarrow O_2 + H_2O \quad (4)$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \text{ (Buxton et al., 1988)} \quad (5)$$

3.4.2. Model-based evaluation

Subsequently, the degradation of the studies acids through UV/H_2O_2 was characterized by a pseudo-first- order kinetic model:

$$Ln\left(\frac{C_0}{C_t}\right) = kt \quad (6)$$

where C_0 and C_t are the initial concentration of organic acids and the concentration of acids at specific time t respectively, k is the pseudo-first-order rate constant (min^{-1}), and t is the reaction time (min).

The rate constants along with the half-lives (ln (2)/k) and the regression coefficients are summarized in Table 4. As shown in Table 4, with increasing H_2O_2 dosage from 25 to 200 mg L^{-1}, the k values increased and consequentially the half-lives of the acids decreased. It should be highlighted that benzoic acid decomposition was faster than other acids in RNS as half-life values of 18, 51 and 83.5 min for BA, PhA and SA respectively were obtained in the presence of 200 mg L^{-1} H_2O_2.

3.5. Effect of inorganic ions

RNS in hydroponic systems consists of essential micro and macro-elements (i.e. K, Ca, Mg, N, P, Fe and S) in the form of inorganic ions such as carbonate, bicarbonate, nitrate, phosphate and sulfate (Hosseinzadeh et al., 2017a). Mineralization of organic compounds in AOP processes might be influenced in the presence of these components (Liao et al., 2001; Hu et al., 2003). Inorganic carbon is known to be a strong hydroxyl radical scavenger in the photocatalytic process.

As shown in Table 5, also the rate constants for the oxidation of most inorganic ions with ·OH radicals are reported to be quite high. Hence, hydroxyl radical scavenging is expected to occur and delay the decomposition rate of the target compounds. Ajmera et al. (2002) found that BA removal efficiency (through photocatalytic degradation on TiO_2) was reduced from 88.7% to 76, 85.5 and 65% in presence of chlorides, sulfate, and nitrate respectively. Riga et al. (2007) reported that decolorization rate was adversely affected in presence of 0.1 M of $H_2PO_4^-$ along with other inorganic ions by the following order: $H_2PO_4^- > HCO_3^- > CO_3^{2-} > SO_4^{2-} > NO_3^-$.

Natural organic matter (NOM) is another parameter which has to be taken into account since root exudates contain a matrix with the great diversity of carbon-based compounds (Hosseinzadeh et al., 2017a). NOM is known to hinder the photodegradation of the organic compounds as NOM is able to absorb UV light leading a reduction in UV transmittance during the oxidation process (He et al., 2013; Zhang et al., 2016). Further, the inhibitory effect of NOM through scavenging of hydroxyl radicals was also reported based on reaction (7) (Gara et al., 2009).

$$NOM + \cdot OH \rightarrow Products \left(k = 2.23 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}\right) \quad (7)$$

In order to gain a deeper understanding of the effects of carbonate and bicarbonate anions along with other ions on the degradation of BA, PhA and SA, a set of experiments were performed. As shown in Fig. 3, the removal of all three acids was affected significantly in presence of anion species in RNS where a 17.2%, 56.1% and 53.5% more removal of the BA, PhA and SA was observed after 90 min respectively in DI water when 50 mg L^{-1} H_2O_2 was used.

3.6. Effect of irradiation time on decomposition efficiency

Based on the results above, it could be concluded that a high of H_2O_2 is optimal for removal of the selected organic acids if an H_2O_2 excess is avoided. For example, at 200 mg L^{-1} a removal in RNS of 97%, 71% and 56% for BA, PhA and SA respectively was obtained after 90 min oxidation. An excess of H_2O_2 might increase the risk of autotoxicity and endanger plant health. To tackle this issue and promote the performance of UV/H_2O_2, the effect of an extended irradiation period on the removal efficiency was also investigated. In order to reduce the risk of autotoxicity (as a result of high-dose H_2O_2 in the RNS), the effect of lower dosages (i.e. 25 and 50 mg L^{-1}) of H_2O_2 in longer time was investigated. Reaction time for long term experiments was set at 270 min since after that no changes in removal efficiency was observed. As seen in Fig. 4, with increasing the reaction time, the removal efficiency for all acids was improved. This observation implies that hydroxyl radicals were not completely consumed in the aqueous solutions after 90 min. Therefore, reaction time was prolonged to compare the effect of increasing the irradiation time in terms of the removal of selected

Table 4
Kinetic parameters of pseudo first order for decomposition of BA, PhA and SA in exposure of 25–200 mg L^{-1} H_2O_2.

[H_2O_2] (mg L^{-1})	k(min^{-1})	$t_{1/2}$ (min)	R^2
BA-RNS			
25	0.0089	77.9	0.96
50	0.0181	38.3	0.97
100	0.0347	20	0.98
200	0.0386	18	0.99
BA-DI water			
25	0.0169	41	0.99
50	0.0475	14.6	0.96
100	0.0726	9.55	0.91
200	0.0842	8.2	0.87
PhA-RNS			
25	0.0028	247.5	0.98
50	0.0051	135.9	0.98
100	0.0095	73	0.99
200	0.0136	51	0.99
PhA-DI water			
25	0.0104	66.6	1
50	0.0307	22.6	0.98
100	0.0647	10.7	0.97
200	0.0766	9	0.96
SA-RNS			
25	0.0037	187.3	0.98
50	0.0046	150.7	0.97
100	0.0064	108.3	0.94
200	0.0083	83.5	0.92
SA-DI water			
25	0.0095	72.9	0.97
50	0.0241	28.8	0.99
100	0.0505	13.7	0.94
200	0.0679	10.2	0.94

Table 5
possible ·OH scavenging reactions in RNS during the UV/H_2O_2 oxidation process.

Reaction	Rate constants ($L\ mol^{-1}\ s^{-1}$)	Ref
CO_3^{2-} ·OH → $CO_3\cdot^-$ OH^-	3.9×10^8	(Buxton et al., 1988)
HCO_3^- ·OH → $CO_3\cdot^-$ H_2O	8.5×10^6	(Buxton et al., 1988)
HPO_4^{2-} ·OH → $HPO_4\cdot^-$ OH^-	–	(Riga et al., 2007)
SO_4^{2-} $OH\cdot$ → $SO_4\cdot^-$ OH^-	3.5×10^5	(Løgager et al., 1993)
HCO_3^- $SO_4\cdot^{2-}$ → $HCO_3\cdot^-$ SO_4^{2-}	2.8×10^6	(Huie and Clifton, 1990)
NO_3^- $SO_4\cdot^{2-}$ → $NO_3\cdot^-$ SO_4^{2-}	5×10^4	(Løgager et al., 1993)

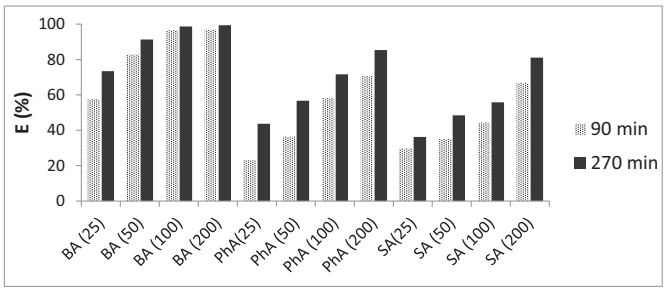

Fig. 4. Comparison of the effect of extending the UV irradiation time at different H_2O_2 dose on organic acids degradation efficiency.

acids. Fig. 4 illustrates that 50 mg L^{-1} H_2O_2 is able to decompose >82% and 91% of BA after 90 and 270 min respectively while inadequate removal efficiency (almost 50%) was observed for PhA and SA even after 270 min reaction. In line with the higher degradation rate of BA compared to PhA and SA, even in the presence of 25 mg L^{-1} a high removal percentage (73.4%) was obtained after 270 min. Hence, it can be concluded that the removal efficiency values obtained for the selected acids in long irradiation time (270 min) and a low dose of H_2O_2 is relatively equal to those obtained in short irradiation time (90 min) and a high dose of H_2O_2.

3.7. Intermediate identification and reaction mechanism for BA decomposition in RNS

In order to identify the intermediates formed during the degradation of benzoic acid in RNS (25 mg L^{-1} of BA), GC–MS analysis at different irradiation times was carried out. The main intermediates were salicylic acid, phenol, 2–3 dihydroxybenzoic acid, 1–2 dihydroxybenzene, maleic acid, oxalic acid and acetic acid. According to Zhong et al. (2017), the degradation mechanism of benzoic acid through ·OH radicals could be explained by following three steps; hydroxylation of benzoic acid to generate aromatic products (i.e. 3-hydroxybenzoic and protocatechuic acids). Next, these products are oxidized to generate ring-opened compounds. Finally, the short-chain aldehydes and carboxylic acids are formed and eventually transformed into CO_2 and H_2O. Based on the information, the degradation pathway for BA was proposed and illustrated in Fig. 5. It is assumed that the aromatic ring might be attacked by hydroxyl radicals and produces an ·OH added compound (i.e. salicylic acid). Further, ·OH radicals are able to attack salicylic acid and generate multi-hydroxyl (two to three OH groups) intermediates. GC–MS analysis revealed the presence of 2–3 dihydroxybenzoic acid and 1–2 dihydroxybenzene. Thereafter, the intermediates were expected to generate ring-opened intermediates such as maleic acid, oxalic acid and acetic acid (Fig. 5).

Among the produced intermediates, salicylic acid was chosen for further investigation since it was detected as the initial and main decomposition product which also evidenced by other researchers (Singla et al., 2004; Sun et al., 2008). On the other hand, based on the literature review, salicylic acid is known to be a plant growth inhibitor for many crops (Hosseinzadeh et al., 2017a). Hence HPLC analysis was employed to quantify the concentration of salicylic acid during the oxidation process. In this approach, the removal efficiency of salicylic acid in the presence of 25 and 50 mg L^{-1} at specified time interval was calculated and shown in Fig. 6. The results showed that, the available ·OH radicals can easily degrade salicylic acid to simpler compounds whereas 74% and 85% removal efficiency was obtained in exposure of 50 and 100 mg L^{-1} H_2O_2 respectively while the degradation efficiency of its parent component (BA) reached to 57.5% and 82.8% (Fig. 4) under the same operating conditions. Further, the pseudo-first-order well represented the experimental data for decomposition salicylic acid during the oxidation process, exhibiting high linear correlation coefficients ($R^2 \geq 0.98$). The k value increased from 0.018 to 0.026 $min^{-1}$when H_2O_2 concentration increased from 50 to 100 mg L^{-1}, displaying the steeper slope for 100 mg L^{-1} compared to 50 mg L^{-1}.

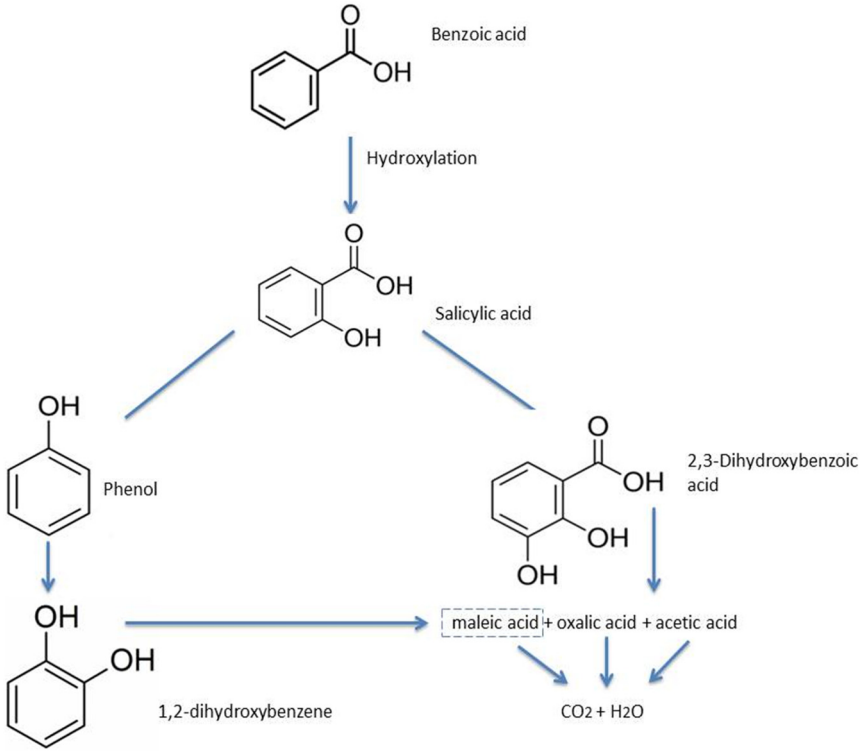

Fig. 5. Proposed degradation pathways of BA during the oxidation process.

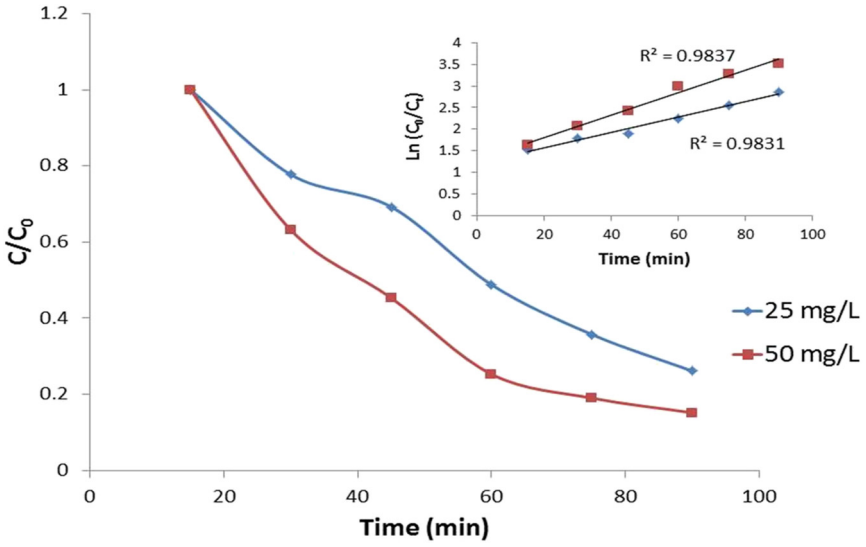

Fig. 6. The degradation of the main identified intermediate (salicylic acid) as a function of H_2O_2 dose when using BA as a parent component.

3.8. Cost analysis

The comparison of the operating costs for the 2 following experimental conditions was undertaken: (i) addition of 50 mg L^{-1} H_2O_2 and UV irradiation for 270 min and (ii) addition of 200 mg L^{-1} H_2O_2 UV irradiation for 90 min. These operating conditions were selected based on the results obtained for benzoic acid removal (shown above) indicating that both are able to decompose 90% of benzoic acid. Since the cost investigations were focusing on operating costs, the investment costs for apparatus and buildings were not taken into account. In this study, chemical (H_2O_2 30 wt%) and energy costs (pump UV lamp) were considered in accordance with their unit costs (H_2O_2: 30 wt%, 0.231 € kg^{-1} and electricity cost 0.12 € kWh^{-1}) obtained from previous research (Chys et al., 2015). Based on the data obtained from the supplier, the respective output power for UV lamp and the pump was 18 W and 24 W respectively.

Based on the unit costs and the consumptions for treatment of one liter sample, the chemical and energy costs were calculated to be 0.012 and 0.023 € when 50 mg L^{-1} H_2O_2 is added and the UV irradiation time is 270 min, while these values were 0.046 and 0.054 euros € when 200 mg L^{-1} H_2O_2 is added and the UV irradiation time is 90 min, indicating that the final operating cost of the UV/H_2O_2 process for low concentration H_2O_2 in longer time is more (over 1.5 fold) cost-effective than the high H_2O_2 concentration in shorter time. Moreover, the low H_2O_2 concentration in longer time reaction, minimize the risk of probable toxicity. As a result, oxidant concentration can influence the total cost significantly as a main factor in comparison with energy cost as it was also evidenced by Zhang et al. (2016). Therefore, the low dose of H_2O_2 (i.e. 50 mg L^{-1}) in longer reaction time can be recommended as a logical choice to meet lower operating costs and prevent autotoxicity occurrence during the process simultaneously.

4. Conclusion

This study investigated the photodegradation of selected root exudates (BA, PhA and SA) in RNS by UV/H_2O_2 process. The results from the present study can be summarized as follows. Firstly, the degradation efficiency of all organic acids was improved with increasing of H_2O_2 concentration from 25 to 200 mg L^{-1} while for higher dose of H_2O_2 (800 mg L^{-1}) a reverse trend was observed. Secondly, the results showed that decomposition of organic acids was significantly hindered in presence of inorganic ions available in RNS. Thirdly, despite 90% decomposition efficiency of benzoic acid was obtained upon 90 min irradiation, only 30% COD removal was achieved implying a majority of organic acids transformed into byproducts rather than complete mineralization. Subsequently, the degradation pathway was proposed based on the identified byproducts. Fourthly, the cost analysis demonstrated that the oxidant (H_2O_2) concentration plays the most significant role in total cost during the oxidation process whereas the desirable operating condition was found to be 50 mg L^{-1} H_2O_2 upon 270 min irradiation. As a result, the present study provides useful information with respect to the oxidation process of organic acids and COD present in RNS.

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